

U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

AD-A028 526

Polarographic Detection of Cd(II) and Cu(II) Ions in Bilge Water

Naval Academy

February 19, 1976

237112

Report USNA-EPRD-19

ADA 028526

POLAROGRAPHIC DETECTION OF Cd(II) and Cu(II) IONS
IN BILGE WATER

Assoc. Professor Frank J. Gomba
Assoc. Professor Morris M. Oldham
Assoc. Professor W. Donald Pennington
Chemistry Department
U. S. Naval Academy
Annapolis, Maryland 21402

19 February 1976

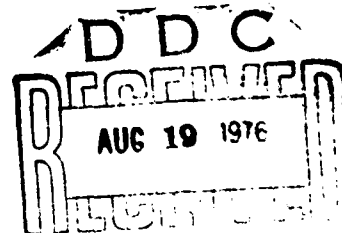
Report for period 1 July 1975 to 1 September 1975

Unlimited Distribution

Prepared for:

Naval Material Command
Office of Support Technology
Environmental Protection, Code 03421
Washington, D. C. 20360

Energy-Environment Study Group
205 Rickover Hall
U. S. Naval Academy
Annapolis, Maryland 21402



REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

DISTRIBUTION STATEMENT A
Approved for public release;
Distribution Unlimited

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER USNA-EPRD-19	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) POLAROGRAPHIC DETECTION OF Cd(II) and Cu(II) IONS IN BILGE WATER.		5. TYPE OF REPORT & PERIOD COVERED Final 1 July 1975 - 1 Sept '75
7. AUTHOR(s) Assoc. Prof. Frank J. Gomba Assoc. Prof. Morris M. Oldham Assoc. Prof. W. Donald Pennington		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS U. S. Naval Academy Annapolis, Maryland 21402		8. CONTRACT OR GRANT NUMBER(s)
11. CONTROLLING OFFICE NAME AND ADDRESS Naval Material Command, Office of Support Technology, Environmental Protection, Code 03421 Washington, D. C. 20360		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 62765N TF 57.572.001
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) Energy-Environment Study Group U. S. Naval Academy, Rickover Hall Annapolis, Maryland 21402		12. REPORT DATE 19 February 1976
		13. NUMBER OF PAGES
		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) UNLIMITED		
<div style="border: 1px solid black; padding: 5px; display: inline-block;"> DISTRIBUTION STATEMENT A Approved for public release; Distribution Unlimited </div>		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) D.C. Polarography, Bilge Water Analysis, Detection of Cd(II), Cu(II), Ni(II)		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This work extends that started in USNA-EPRD-2, February 1974 where d. c. polarography was used to detect certain heavy metal ions in sea water. The detection of copper, cadmium, and nickel ions in bilge water is presented in this paper.		

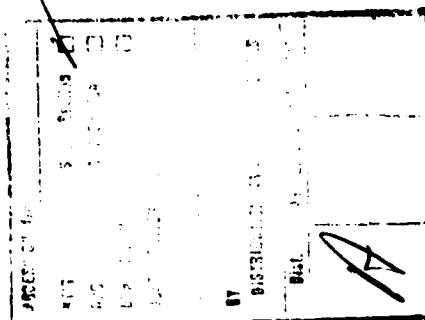
PREFACE

This work was an outgrowth of the work done by Midshipman S. Diamond & Professor J.H. Klein (USNA-EPRD-2), and Professors W.D. Pennington & J.H. Klein (USNA-EPRD-7) where the d.c. polarographic method of analysis was found suitable for the detection of certain heavy metal ions in sea water at concentrations as low as 1 ppm. This success led to an attempt to extend the method to include the detection of Cd(II) and Cu(II) in bilge water samples and perhaps Cr(VI) in sea water (not established earlier).

The toxicity of Cd(II) and Cr(VI) has been demonstrated in respect to mammalian cells and synergistic toxicity of Cu(II) and Zn(II) has been noted, e.g. in Bioassay Techniques and Environmental Chemistry, Gary E. Glass, editor, p. 217. Copper, of course, is a constituent of many alloys used in ship piping systems and corrosion in such systems would place the copper ion in bilge water discharge as a contaminant.

The bilge water composition may vary greatly, but it may include oil, miscibly dispersed, which may interfere with any polarographic analysis.

In addition to the detection of Cu(II) and Cd(II) in bilge water, the detection of Ni(II) in bilge water was also attempted. And finally, the effect of the addition of known concentrations of Navy Distillate coupled with known additions of Type I Detergent in the polarographic detection of Cd(II) in distilled water



was also investigated. The latter was stimulated by work done by S.P. Massie involving ultra- violet spectrophotometric studies of sea water samples containing Type I Detergent (USNA-EPRD-23).

EXPERIMENTAL

1. Apparatus and Reagents

A Heath Built EVA 19-2 direct current polarograph was used with a Heath Built EVA 19-6 dropping mercury electrode assembly with a three electrode system. Polarograms were made on a Beckman 10-inch recorder. All pH measurements were made with a Orion Model 701 pH meter. Supplies of bilge water were obtained at the Naval Base at Rota, Spain.¹ All reagents used were of analytical grade or better. Distilled water used was doubly distilled, the second distillation using an all glass Kontes Model WS-2 still.

The polarograph was calibrated using 100 ppm Cd(II) solutions ($\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ in 0.1M KCl) as the supporting electrolyte, giving an $E_{1/2}$ of $0.595 \pm 0.005\text{V}$ vs SCE. The open circuit drop time was 3.71 seconds and the m value $2.336 \pm 0.001 \text{ ng/sec}$, using a 50cm head of mercury. To avoid pH adjustments of test samples, an $\text{NH}_4\text{Cl} - \text{NH}_3$ buffer solution was used, which also served as the supporting electrolyte. Freshly prepared gelatin solutions were made daily for use as a maximum suppressor.

2. Preliminary Polarograms of Bilge Water Samples

A 25 ml aliquot of 100 ml solutions containing 90 ml of bilge water and 10 ml of 1M $\text{NH}_4\text{Cl} - \text{NH}_3$ was used with 2 drops of 2% gelatin added as a maximum suppressor.

¹Klein, Joseph H. and W.D. Pennington, "Examination of Contaminated Sea Water for Copper Ion Using Direct Current Polarography," USNA-EPRD-7, Jan 1, 1974-Sept 1, 1974.

Of the twelve (12) bilge water samples tested only three gave any discernible wave in addition to that obtained using only buffer and gelatin alone. These samples were from the following ships: U.S.S. Alacrity, U.S.S. Assurance, and U.S.S. Fiske. None of these had an $E_{1/2}$ in the vicinity of that expected for either Cd(II) or Cu(II) as judged from literature values in either distilled water supporting electrolyte or sea water samples. Further analyses of these samples above will be mentioned later. The other bilge water samples were mixed to serve as a common source of bilge water.

Each sample of bilge water was filtered to remove any suspended solids and/or oil. This was found later to be unnecessary if the samples were allowed to stand so that aliquots could be taken free from suspended solids and past any oil layer. If any colloidal suspension of oil was present in these samples, they did not show any interference on the polarographic waves.

Some bilge water filtered did leave appreciable quantities of residue. Three residue samples were tested for the presence of iron and copper as Fe(III) and Cu(II). The iron test was the Rollins-Oldham method using PDT (USNA-EPRD-12) and the copper analysis was made by the spectrophotometric method employing Bathocuproine (2, 9 -Dimethyl- 4,7 diphenyl 1-1, 10-phenanthroline). The range of Fe(III) was from 0.642-11.62 ppm and the range for Cu(II) was 1.27 -10.8 ppm.

3. Determination of Cd(II) and Cu(II) in Bilge Water

Since the bilge water samples did not show the polaro-graphic presence of any Cd(II) or Cu(II), known

quantities of these ions were added to the bilge water to ascertain their detection polarographically.

Standard solutions of both Cd(II) and Cu(II) were prepared by dissolving 1.0000 gram of each metal (99.99%) in sufficient concentrated nitric acid to affect solution. These solutions were then diluted to one litre with distilled water providing standard solutions with a concentration of 1000 ppm in Cd(II) and Cu(II), respectively. Aliquots of these solutions were used with the mixed bilge water samples and supporting electrolyte-buffer to make solutions of 1, 5, 10 and 20 ppm in either Cd(II) or Cu(II).

In the case of Cu(II) solutions, two waves were formed. Because of the shape and position of the first wave, a good estimate of its $E_{1/2}$ was not attempted, using the second and better formed wave to establish an $E_{1/2}$. The first wave can be attributed to the reduction of $\text{Cu(II)} \rightarrow \text{Cu(I)}$ (as ammonia complex) and the second wave to the reduction of $\text{Cu(I)} \rightarrow \text{Cu(0)}$. The wave heights were nearly equal due to both involving a one-electron reduction. The $E_{1/2}$ of the second copper wave was -0.377 ± 0.010 volt vs S.C.E.

The Cd(II) samples all gave one well defined wave attributable to the two-electron reduction of $\text{Cd(II)} \rightarrow \text{Cd(0)}$; the Cd(II) being complexed with ammonia. The $E_{1/2}$ was -0.676 ± 0.004 volts vs S.C.E.

Plots of i_d vs concentration, in ppm, for each ion showed that a good estimate could be made of any Cd(II) in bilge water samples, treated as above, provided the concentration is not below 1 ppm. While a maximum of 20 ppm was used in these tests, this does not imply this is

the maximum concentration detectable by polarographic means, but this maximum was used as most bilge water samples would probably rarely exceed this value.

See Figure 1 for plots of i_d versus ppm for both Cu(II) and Cd(II). Each point represents the average of at least three runs.

4. Determination of Ni(II) in Bilge Water

Because of the availability of both time and bilge water samples, it was decided to further ascertain if Ni(II) could be determined, by d.c. polarography, in bilge water. Preliminary runs on bilge water samples did not show the presence of any Ni(II) and thus a standard solution of Ni(II) was prepared which served as the source of Ni(II) to be deliberately added to bilge water samples as was done with both Cd(II) and Cu(II).

A standard Ni(II) solution, prepared in the same manner as were standard solutions of both Cd(II) and Cu(II) was used to make test samples of 1, 5, 10 and 20 ppm Ni(II). All other conditions were the same as with the Cd(II) and Cu(II) samples in bilge water.

While well defined waves due to the two-electron reduction of Ni(II) (as the ammonia complex) were formed, the i_d vs ppm plot for Ni(II) indicated that this method is probably better suited for concentrations of 5 ppm Ni(II) or above (see Fig. 1). The $E_{1/2}$ was -0.936 ± 0.016 volts vs S.C.E.

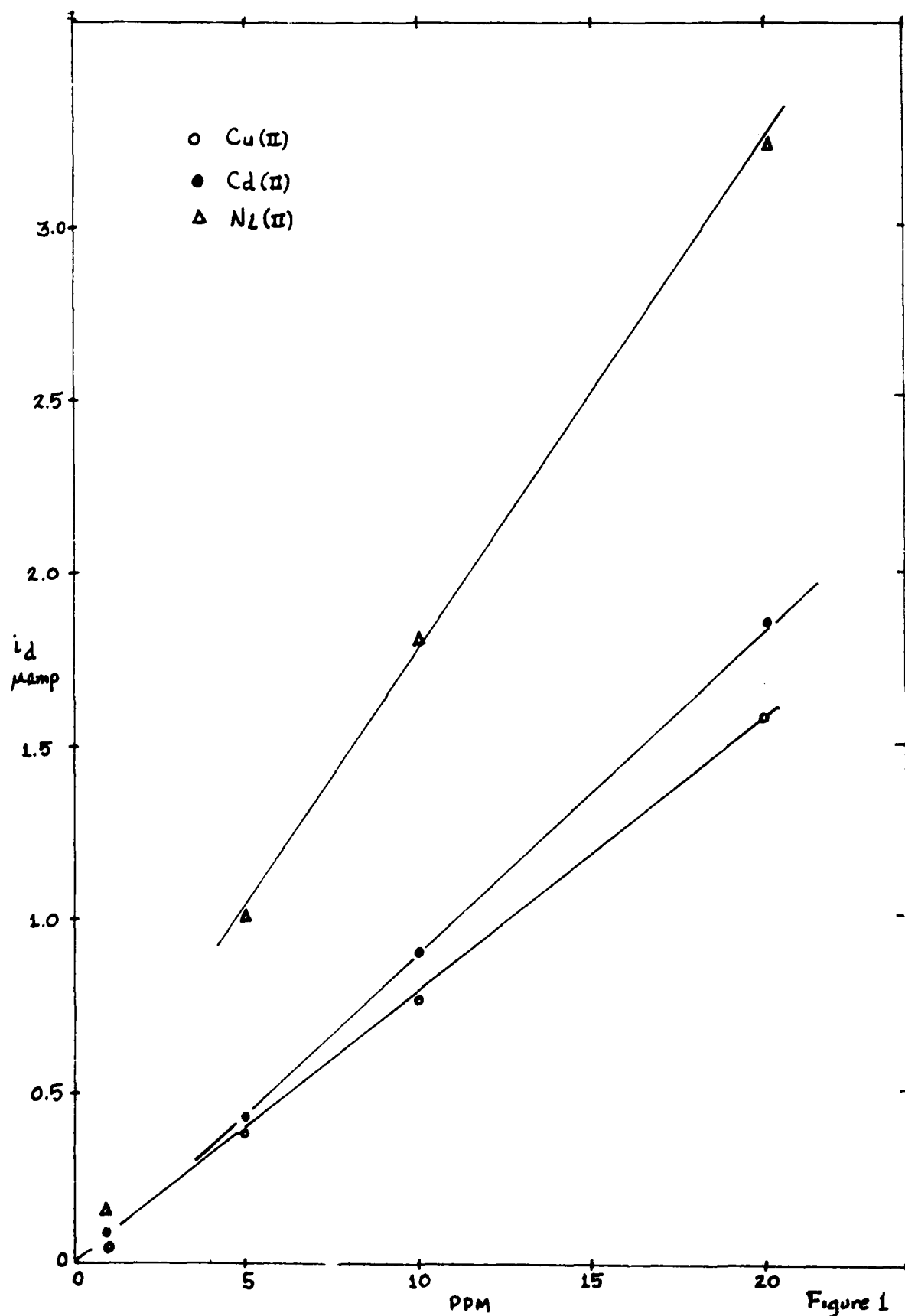


Figure 1

The simultaneous determination of the presence of Cu(II), Cd(II), and Ni(II) in bilge water samples is possible as well.

5. Determination of Cr(VI) in Sea Water

Since the investigations of Klein and Diamond², and Klein and Pennington¹ did not indicate the detection of any chromium species in sea water, this work was extended to include the feasibility of using the polarographic method to determine chromium in sea water.

The form of chromium species in aqueous solution is known to depend upon the pH. At pH's below the pKa of 3.9 for the hexaaquo ion $\text{Cr}(\text{H}_2\text{O})_6^{3+}$, the predominant form of chromium is the hexaaquo ion. But at pH's above this value dimers and other hydroxy species may exist which can complicate the polarogram. Since the pH of sea water hovers around 8, the chromium would probably not exist as one clearly defined specie. It was decided that at the pH of the test solutions used in the bilge water cases, about 9.2, using the $\text{NH}_4\text{Cl}-\text{NH}_3$ buffer, that perhaps the detection of $\text{CrO}_4^{2-}(\text{Cr}[\text{VI}])^3$ could best be done in sea water samples. The sea water samples were thus prepared using a standard $\text{K}_2\text{Cr}_2\text{O}_7$ solution (99.999%) which was treated with NaOH to convert the dichromate to chromate. The sea water itself was obtained about one mile offshore from Wrightsville Beach. Solutions of 1, 5, 10 and 20 ppm were then prepared for polarographic runs.

¹Ibid.

²Klein, Joseph H. and Steven Diamond, "Simultaneous Determination of Zinc, Lead and Cadmium Ion Concentration in Contaminated Seawater Using Direct Current Polarography," USNA-EPRD-2, Dec. 1973.

Because of the known difficulties encountered in the polarographic study of CrO_4^{2-} ions,³ it was found that more well defined waves were obtained without using gelatin, which allowed the electrode reaction to take place more efficiently. A plot of i_d vs ppm Cr(VI) show that an estimation of the concentration of Cr(VI) is better at concentrations in the 1 to 10 ppm range (see Fig. 2). The $E_{1/2}$ was -0.279 ± 0.003 volt vs S.C.E.

6. Further Polarographic Study of the Bilge Water Samples from U.S.S. Fiske, U.S.S. Alacrity, and U.S.S. Assurance.

These bilge water samples did, as mentioned earlier, give a discernible wave when tested.

	Bilge Water From	$E_{1/2}$, v	i_d , μa
(1)	U.S.S. Alacrity	-1.45	0.10
(2)	U.S.S. Assurance	-1.53	0.18
(3)	U.S.S. Fiske	-1.23	0.10

A check of $E_{1/2}$'s in $\text{NH}_4\text{Cl}-\text{NH}_3$ buffer indicated that the ion responsible may be Zn(II).

A sample of U.S.S. Fiske bilge water was treated with 10 ppm Zn(II) and the wave height increased, showing at least qualitatively that zinc ions are present in this bilge water sample; probably no higher than 1 ppm.

The other two bilge water samples gave polarographic waves which, in a preliminary test, could be due to the presence of Co(II), since the wave was enhanced at -1.5

³Miller, I.R., "Problems in the Polarography of Chromates," J. Electroanal. Chem., Vol. 15, p. 49 (1967).

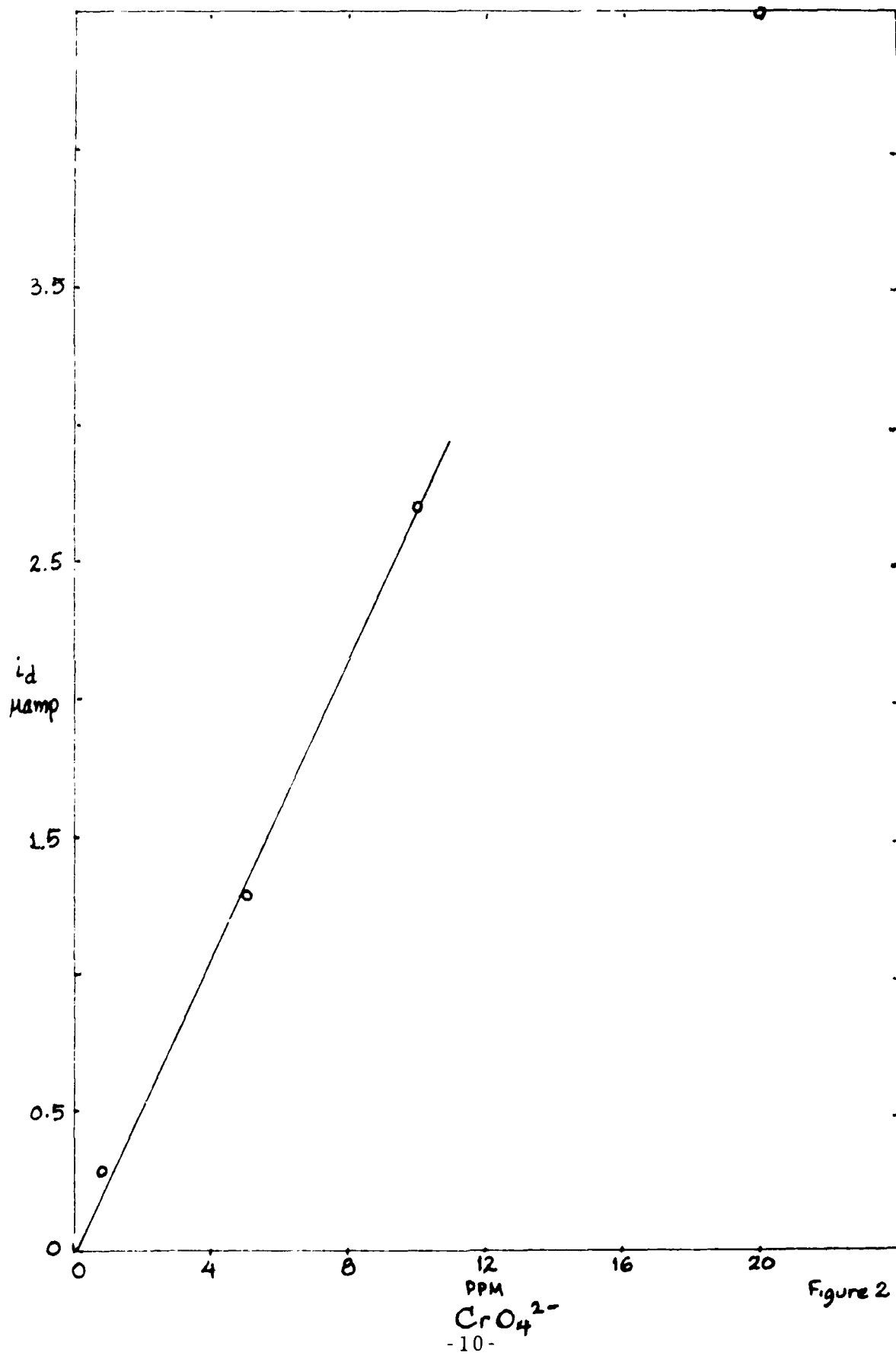


Figure 2

volts, when Co(II) was deliberately added to the bilge water samples.

7. Polarographic Examination of Type I Detergent in Distilled Water.

While performing these investigations on bilge water, another investigation in the same laboratory was being done by S. P. Massie on Type I detergent. This detergent is used by the Navy in treating bilge water to emulsify any oil present in the bilge water.

At first it was assumed that perhaps the excess detergent may be detected polarographically and may have been responsible for the small wave in the three bilge water samples mentioned earlier. While the addition of Type I detergent to these bilge water samples did not increase the wave height (even with 100 ppm detergent present), further polarographic tests were made with Type I detergent and Navy Distillate (Mil F-24397) to see if the detergent efficiency in emulsifying this fuel oil could be seen.

As expected, oil samples in distilled water gave erratic waves, but were noticeably smooth when the detergent was added. In fact, in these preliminary tests, using 10 ppm Cd(II) in distilled water - ammonium chloride-ammonia buffer solutions, the wave due to the reduction of Cd(II) was well formed with detergent and oil added [see Fig. 3 (a), (b)].

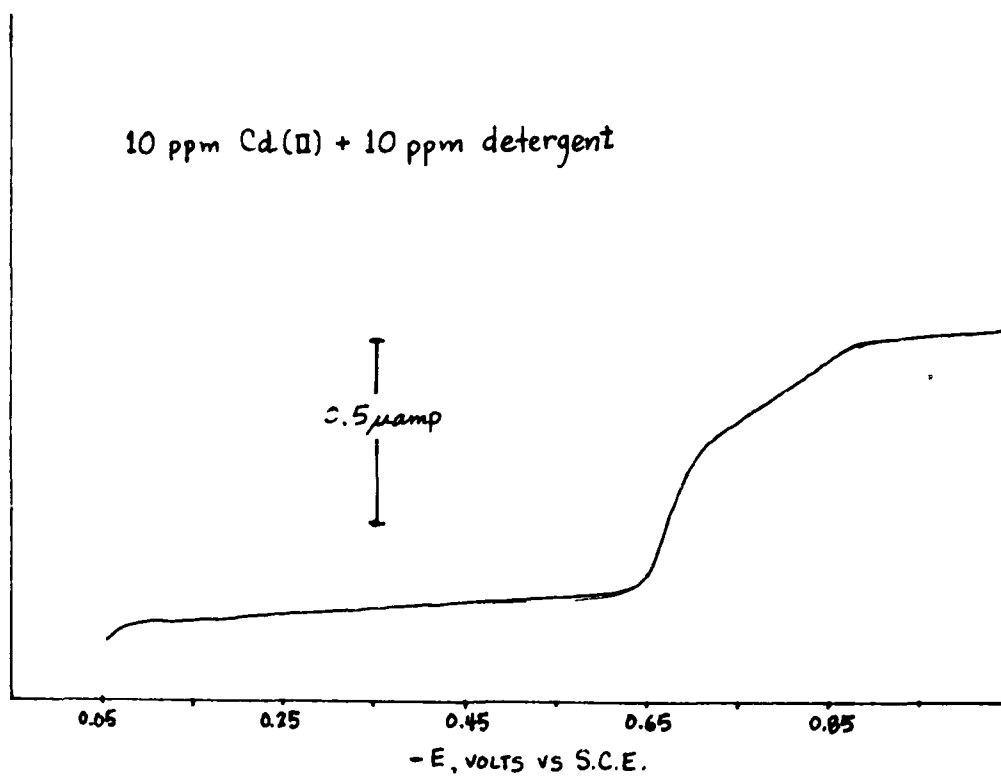


Figure 3a

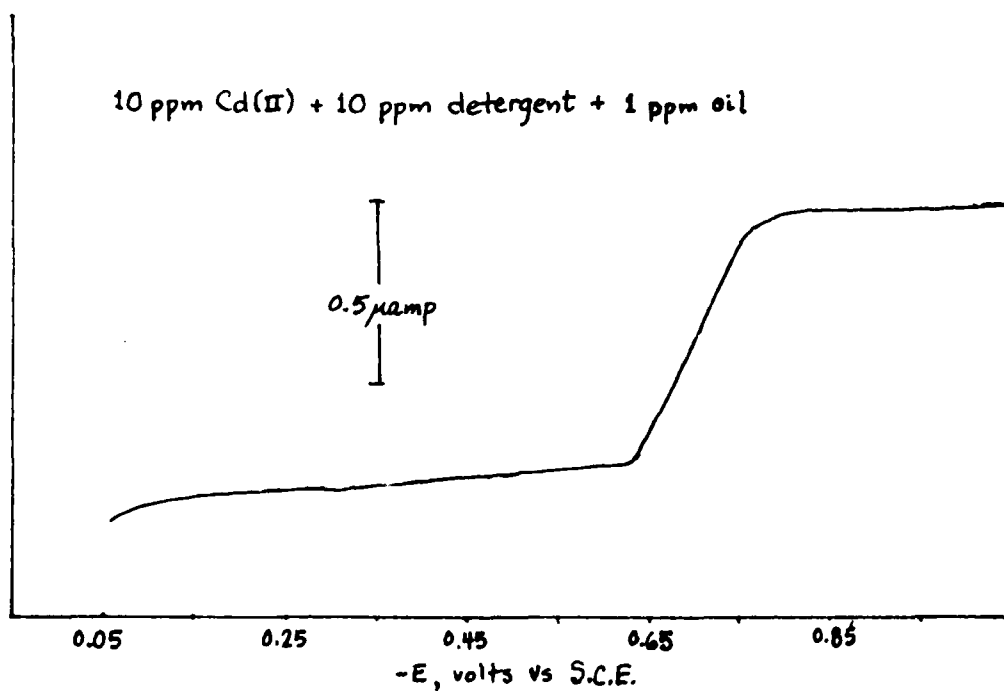


Figure 3b

Conclusions and Recommendations

This work indicates that Cu(II), Cd(II) and Ni(II) can be qualitatively identified and their concentrations estimated in bilge water at concentrations above 1 part per million [above 5 ppm for Ni(II)].

This method (d.c. polarography) is rapid and does not require extensive prior sample treatment as long as the bilge water aliquot taken is free from suspended solids and nonmiscible oil.

It is possible to detect any metal ion of interest in bilge water samples by this method if its detection is possible in sea water with allowances made for possible interfering ions ($E_{1/2}$'s within about 150 mV of that of the ion in question) and provided that the concentrations are not less than 1 ppm. The use of a buffer is recommended to ensure a rapid, reproducible pH value as well as maintaining a single ionic species in solution. The buffer, if properly selected can then serve as the supporting electrolyte.

This work involving the detection of Cd(II) in distilled water in the presence of Navy Distillate and Type I Detergent should be further investigated. This method may be well suited for the detection of either Navy Distillate and/or Type I Detergent in sea water and/or bilge water samples. It may prove to be a rapid method for the detection of these substances and for the rapid determination of the efficacy of detergents in tying up oils which may find their way into bilge water and/or sea water.

APPENDIX 1.

LIST OF SHIP SOURCES OF BILGE WATER

(Collected by J.H. Klein, Rota Spain, USNA-EPRD-2)

1. USS Assurance
2. SS American Trader
3. USCG Chase
4. USCG W33 Duane
5. M/N Falcon Duchess
6. Harold J. Ellison DO2641
7. USS Fiske
8. USS Ingham
9. USNS Kane
10. USS Mahoa
11. USS Shahaska
12. USS Tallula

REFERENCES

1. Klein, Joseph H. and W.D. Pennington, "Examination of Contaminated Sea Water for Copper Ion Using Direct Current Polarography," USNA-EPRD-7. Jan. 1, 1974-Sept. 1, 1974.
2. Klein, Joseph H. and Steven Diamond, "Simultaneous Determination of Zinc, Lead and Cadmium Ion Concentration in Contaminated Sea Water Using Direct Current Polarography," USNA-EPRD-2, July 1, 1973 - Dec. 29, 1973.
3. Miller, I.R., "Problems in the Polarography of Chromate," J. Electroanal. Chem., Vol. 15, p. 49 (1967)
4. Rollins, O.W. and Morris M. Oldham, "Spectrophotometric Determination of Copper at Low Levels in Fresh or Saline Waters," USNA-EPRD-4, July 1, 1973 - Jan. 1, 1974.